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FATE OF OCEAN DUMPED ACID-IRON WASTE IN A MERL STRATIFIED MICROCOSM

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ABSTRACT

Field studies have provided information on the short-term effects of acid-iron waste disposal at a deep water dumpsite off the coast of New Jersey. To assess the long-term effects of the acid-iron waste, an experiment was conducted at the MERL facility (Marine Ecosystems Research Laboratory) of the University of Rhode Island. The MERL tanks (2 m diameter and 5 m deep) provide planktonic ecosystems for experimental manipulation. To simulate conditions at the deep water dumpsite, two MERL tanks were established with a 10°C temperature differential maintained between the surface and bottom layers. Acid-iron waste was added to the surface layer of one of the tanks at a 10^5 dilution. The decay of iron from the surface layer of the tank and the penetration of the iron floc through the thermocline was followed as a function of time after the waste addition. The removal of iron from the surface layer was first order with respect to iron with a half life of 35 hr. The mechanism of iron removal was gravitational settling of the iron floc and not assimilation by phytoplankton and zooplankton species exposed to acid-iron waste. The results of the MERL tank experiment were consistent with field observations of an actual acid-iron waste dump.

1. INTRODUCTION

Disposal of waste material in the ocean without detrimental effects has become an important area of marine research. For the past few years we have investigated the effects of dumping industrial wastes at a deep water dumpsite located off the coast of New Jersey, DWD-106 (Brown et al., 1982; Kester et al., 1981). The depth of the water column at DWD-106 is about 2000 m and therefore the primary fate of wastes is dispersion in the water column rather than incorporation into the sediments. An acid-iron waste obtained from the production of titanium dioxide at the Dupont Edge Moor facility (Edge Moor, Delaware) has been dumped at DWD-106 since 1977. This liquid waste is discharged into the water column from a towed barge; there is a rapid 10^5 dilution of the waste in the wake of the barge. Subsequent oceanic mixing processes are slow and have been predicted to require weeks or months for a ten to hundred fold dilution of the acid-iron waste plume (Csanady, 1981; Mukherji and Kester, 1981).

The chemical constituents of the acid-iron waste are listed in Table 1. As this waste mixes with seawater the acid is rapidly neutralized by the carbonate and borate buffers in seawater and hydrous ferric oxide precipitates. The horizontal dispersion of the waste plume has been tracked by continuous real time measurements of elevated iron concentrations in seawater (Brown et al., 1982).

Our field studies to date have provided detailed information on the short term fate of the acid-iron waste in the marine environment, but they have not revealed the long term effects of the waste in the ocean. Specific questions that have not been resolved include:

Table 1. Comparison of the chemical properties[a] of E. I. duPont deNemours and Co. Edge Moor waste and seawater in which it will be discharged. Based on a 10 September 1976 EPA, Region III, Discharge Permit Application (From Kester et al., 1981).

Property	Waste	Seawater[b]
Density (g ml^{-1})	1.15	1.02
Total Dissolved Solutes (g $liter^{-1}$)	240	35
Total Suspended Solids (g $liter^{-1}$)	1.5	0.001
pH	0.01	8.2
Alkalinity (equivalent $liter^{-1}$)	-4.50	0.002
Chloride (molar)	5.36	0.55
Sulfate (molar)	0.0083	0.029
Hydrogen ion (molar)	0.98	6×10^{-9}
Iron (molar)	0.90	$< 1 \times 10^{-8}$
Titanium (molar)	0.063	$< 1 \times 10^{-8}$
Aluminum (molar)	0.063	$< 1 \times 10^{-7}$
Manganese (molar)	0.031	$< 1 \times 10^{-8}$
Vanadium (molar)	0.004	$< 4 \times 10^{-8}$
Chromium (molar)	0.004	$< 2 \times 10^{-8}$
Lead (molar)	0.0002	1.4×10^{-10}
Total Organic carbon (mg $liter^{-1}$)	960	1

[a] The data in this table for the waste are not internally consistent. Charge equivalents of cations and anions are not equal and the alkalinity is not fully accounted for by the hydrogen ions and iron. The pH may be inaccurate if it was measured by an instrument which does not permit pH < 0. Consequently, the hydrogen ion molarity which appears to be derived from pH may be in error. If the alkalinity is accepted as being correct the hydrogen ion concentration may be calculated by difference. The Fe contributes -2.70 equivalent $liter^{-1}$ and other metals (Al, Mn) provide about -0.2 equivalent $liter^{-1}$. Thus H^+ could be about 1.6 equivalent $liter^{-1}$ in which case the pH would be -0.2.

[b] Wilson (1975); Brewer (1975).

1. What is the ultimate fate of the acid-iron waste in the ocean? Vertical profiles obtained when an acid-iron waste plume was tracked for over 50 hrs after a dump did not show the waste beneath the seasonal thermocline. A constant horizontal diffusion velocity model applied to our field data predicted that iron concentrations in the waste plume should persist at detectable limits ($\geq$ 0.02 μM/kg) for several weeks after the dump. However, in our field studies we have not been able to track the waste plume for more than one or two days after a dump.
2. Are there detrimental effects on the phytoplankton and zooplankton species exposed to the chemical constituents in an acid-iron waste plume for extended periods of time after a dump?

To address these questions a new approach was undertaken. An experiment was conducted at MERL (Marine Ecosystems Research Laboratory) at the University of Rhode Island. MERL is a special facility which provides small scale controlled planktonic ecosystems for experimental manipulation.

2. EXPERIMENTAL

The MERL tanks are 2 m in diameter and 5 m deep containing a 30 cm layer of sediment and associated benthic organisms collected from lower Narragansett Bay. The sediments did not have a direct role in our considerations of acid-iron waste behavior at DWD-106, but they were important to maintain the nutrient regeneration processes

required to sustain the planktonic ecosystem. The tanks were initially filled with water (~30°/₀₀ salinity, 18°C) from Narragansett Bay along with the prevailing population of phytoplankton and zooplankton. The tanks were not inoculated with additional plankton. The tanks were operated as closed systems except to replenish them with water from the bay to maintain the water level in the tank.

Our field studies indicated that the pycnocline plays a major role in the behavior of the acid-iron waste. Two of the MERL tanks were modified to establish a thermocline with one serving as a control and the other as an experimental tank (Klos and Donaghay, 1982). The top 2 m of the water column were maintained at ambient temperature (18-19°C) while the bottom 2 m of water were cooled with heat exchangers to produce a 10°C temperature differential between the surface and bottom layer (Fig. 1). Preliminary experiments with the cooling and mixing parameters of the tanks established that the position and thickness of the thermocline could be altered by changing the position of the heat exchangers and the mixing bars. Throughout the course of this experiment the thickness of the thermocline was 0.5 m with only minor fluctuations from the 10°C temperature differential between the surface and bottom layer. There were no substantial differences in the physical characterisics between the control and experimental tanks.

In order to monitor any mixing across the thermocline that could also transport acid-iron waste, we added NaCl (Baker Analyzed Reagent) to the bottom layer to increase the dissolved salts by about 3°/₀₀. This NaCl also enhanced the pycnocline. Temperature and salinity

profiles of the experimental and control tanks were made daily using a conductivity, salinity and temperature probe (Model 33, Yellow Springs Instrument Co., Yellow Springs, Ohio). Discrete salinity samples of the surface and bottom water were drawn at biweelky intervals in both the experimental and control tank. A detailed vertical salinity profile was made using discrete samples at the middle of the experiment in the experimental tank (Fig. 2). All discrete salinity samples were analyzed using an inductive salinometer (Industrial Instruments, RS-7B).

Acid-iron waste was added to the experimental MERL tank to achieve a 10^5 dilution of the waste in the surface mixed layer. This simulates the conditions observed in the field after the initially rapid dilution of the surface plume. To avoid extreme pH changes as the acid-iron waste was added to the experimental tank, the waste was diluted 100:1 with bay water prior to the addition to the tank. Two additions of acid-iron waste were made within the first 24 hr of the experiment since an initial objective was to maintain a 10^5 dilution of the waste in the surface water for an extended period of time. However, the removal of iron from the surface layer was so rapid after each waste additon that we decided to observe the removal process with time rather than continue with daily additions. The first two additions of waste will be referred to as the first experiment. A third waste addition was made when the iron concentration in the surface layer of the experimental tank returned to background levels (0.17 µM/kg) and this constituted the second experiment. The walls and exposed surfaces in the experimental tank were not cleaned

between the first and second experiment.

The fate of acid-iron waste in the experimental tank was assessed by measuring the total iron concentration as a function of time. The water samples for chemical analyses were obtained using a Teflon sampling tube. Water samples were siphoned directly into the sample bottle to avoid contamination. Measurements for total iron and total chromium were made by atomic absorption spectroscopy (AAS) using a Perkin Elmer Model 5000 spectrophotometer. Due to the high concentration of metals, preconcentration was not necessary; the seawater sample was injected directly into a graphite furnace.

Total iron concentrations from the field study were determined from real time iron measurements using a continuous flow analyzer (CFA, Scientific Instruments, Pleasantville, N.Y.) with a colorimetric technique (Stookey, 1970). Results obtained using the CFA have been shown to be comparable with results obtained using AAS (Brown et al, 1982).

3. RESULTS

3.1. Surface Layer Removal

Vertical profiles of the distribution of iron at several time intervals during the second experiment were made to determine the behavior of acid-iron waste in the experimental tank (Fig. 3). In the first profile obtained 6 hr after the acid-iron waste addition, the concentration of iron in the surface layer increased from a background level of 0.17 μM/kg to 8.1 μM/kg with an accumulation of iron observed at the top of the pycnocline. Twenty hours after the waste

addition the concentration of iron in the surface mixed layer decreased to 3.1 μM/kg with an apparent transport of the iron maxima into the center of the thermocline. The time sequence of vertical iron profiles in the experimental tank showed a steady depletion of iron in the surface mixed layer with the iron levels reaching backgrond levels 236 hr after the waste addition. The structure in the thermocline persisted for 44 hr after the dump; thereafter we observed a smooth iron gradient through the thermocline. The behavior of iron in the bottom water was complicated by the occurence of sediment resuspension, which will be discussed in detail later. However, iron levels in the bottom water showed a marked increase to 2.7 μM/kg 20 hr after the waste addition with a subsequent decrease to background levels 236 hr after the addition.

The removal of iron from the surface layer of the experimental tank during the first and second experiments followed an exponential decay (Fig. 4a) suggesting the removal of iron from the surface mixed layer was first order with respect to iron. A first order kinetic removal process follows the relationship:

$$\ln (Fe(i)/Fe(t)) = k_1 t \qquad (1)$$

where Fe(i) represents the initial concentration, Fe(t) the concentration after time, t, and k_1 is the rate constant for the removal process. A plot of ln (Fe(i)/Fe(t)) vs time for the results of both experiments showed a linear relationship with some scatter. The rate constant for the removal process was calculated from a linear

regression of the observed data using equation (1). A rate constant of 0.0205 hr^{-1} was used to calculate the curve representing iron removal as a function of time (Fig. 4a). The half life of iron, τ, in the surface water was calculated using the relationship:

$$\tau = \ln 2/k_1 \qquad (2)$$

For these data τ = 34 hr.

A closer examination of the removal rates showed that there was a more rapid removal of iron from the mixed layer in the first 50 hr of the second experiment relative to the first experiment. Analysis of the results of the first experiment showed that the removal process is clearly first order with respect to iron; the half life of iron in the surface layer is 31 hr. For the second experiment the removal process was not simply first order in iron; a two step process was indicated by the experimental data (Fig. 4b). Initially there was a rapid removal of iron from the mixed layer; the half life for this removal process was 14 hr. The secondary removal process was slower with a half life of 65 hr.

The visual behavior of the iron floc formed after the acid-iron waste addition was different in these two experiments. In the first experiment large floculant particles of iron were visually evident in the surface layer; these particles grew to several millimeters within the first 36 hr of the experiment. After ~ 36 hr large particulate iron floc was not visible in the surface water and there was a distinct increase in the clarity of the surface water. In this experiment there was minimal adsorption of iron floc on the walls and

exposed surfaces of the tank. This behavior was in contrast to that observed in the second experiment. There was extensive accumulation of the iron floc on the walls and surfaces in the tank ~ 10 hr after the acid-iron waste addition. Any disturbance of the surface would dislodge the iron floc from the surface. For this reason an accurate assessment of the amount of iron on the surfaces could not be obtained from the fouling plates that were suspended in the tank for this purpose. The iron floc particles in the surface water were not as large as those observed in the first experiment. Within 36 hr after the waste addition in the second experiment the iron floc had desorbed from the surfaces and the clarity of the surface water was similar to that observed in the first experiment. The adsorptive loss of iron observed in the second experiment could account for the two step removal process of iron observed in that experiment.

It is not evident why the two experiments showed somewhat different results. The same acid-iron waste was used and the same technique of addition was used in both experiments. The differences between the two experiments were greatest during the initial 10 hr. Over the longer time period of the observations (100 - 300 hr) the results were more similar. It is possible that the first experiment modified some properties of the exposed surfaces in the tank thereby resulting in a different flocculation process during the early stages of the second experiment. A thin organic film was observed on the exposed surfaces of the tank after the first experiment and these coated surfaces were more susceptible to the adsorption of the iron floc.

3.2. Sub-Pycnocline Accumulation and Removal

The behavior of iron in the bottom layer beneath the pycnocline was complicated by the occurrence of a number of high concentrations which did not appear to be related to the acid-iron waste. These high values may represent resuspension of bottom sediment due to the mixers and/or the benthic organisms. Iron levels in the control tank varied from 0.6-1.0 μmole Fe/kg within the first 250 hr of the experiment (Fig. 5a). These control values are consistent with the iron levels observed in the experimental tank prior to the first waste addition. At 165 hr after the start of the second experiment, the control tank contained 2.3 μmole Fe/kg in the deep layer. This high value is not an analytical artifact; it occurred in three samples taken from the bottom layer. Evidently, there are processes which can occur in the sediments that can triple the iron concentration in the bottom layer of the tanks and which obviously are not related to the addition of acid-iron waste.

An event producing high iron concentrations (1.7 to 1.8 μmole/kg) occurred in the experimental tank near the end of the first experiment (235 hr after the first waste addition) and persisted into the early stage of the second experiment (1 to 6 hr after the final addition). The results for the first experiment indicate that elevated iron concentrations observed within the first 10 hr after the waste addition are not related to the vertical flux of acid-iron waste from the surface layer (Fig. 5a). There is a two to three-fold increase in the iron levels in the bottom layer as the acid-iron waste penetrates the thermocline with a subsequent decay to background levels 250 hr after

the addition. An anomalous high iron concentration observed 160 hr in the second experiment suggests an input of iron from bottom resuspension. However this observation cannot be confirmed because of the limited sampling in this time period.

This interpretation of the behavior of iron in the bottom layer can be tested by its consistency with a similar analysis of the behavior of chromium (Fig. 5b). The acid-iron waste contains appreciable concentrations of chromium and we can expect that when the high iron concentrations in the bottom layer are produced by the waste, we should also find high chromium concentrations. The background chromium concentrations were in the range of 2 to 4 nmole/kg. Concentrations two to three times this level were observed at 40 hr after waste addition in the first experiment and 20 hr after addition in the second experiment. These high values subsequently decayed to background at about the same rate as the iron concentrations. The similarity of the iron and chromium data during the period of 20 to 100 hr after waste addition substantiates our interpretation that the waste was present in the water column beneath the pycnocline during this period. The waste subsequently diminished from the bottom layer over a time span of about 60 hr.

3.3. Cross Pycnocline Mixing

An alternate source of iron to the bottom water of the experimental tank is from mixing of the surface and bottom water across the pycnocline. The addition of NaCl to the bottom water changed the salinity of this layer by $\sim 3^{\circ}/_{\circ\circ}$; this salintiy difference can be

used as a conservative tracer to determine the transport of iron from the surface to the bottom water due to mixing. In the 480 hr (20 day) period of this experiment the salinity of the bottom water of the control tank decreased from 33.71°/₀₀ to 33.46°/₀₀ or 0.25°/₀₀ in 20 days The salinity change in the control tank for the same time period was 0.41°/₀₀. The slightly greater salinity change in the control tank was probably due to the loss of ~ 400 liters of water from the thermocline that resulted from a leak in a valve on the control tank midway through the experiment. The salinity of the surface water in both tanks showed more erratic behavior due to the input of fresh rainwater and loss due to evaporation. Also, bay water was added to the surface layer of both tanks prior to the second experiment to maintain a constant water level in the tanks.

The salinity change with time in the experimental tank can be used to estimate the flux of iron from the surface layer to the bottom layer due to mixing across the thermocline. The change of salinity as a function of time can be determined from the slope of the regression line obtained from a plot of salinity vs time. Assuming the volume of surface water and bottom water that are exchanged across the thermocline are equal, the salinity change in the bottom water can be used to calculate the volume of surface water that must be mixed with bottom water using the relationship:

$$V_{mix} = \frac{V_{bot} \ \Delta S°/₀₀bot}{\overline{S}°/₀₀surf - S°/₀₀init\ bot} \qquad (3)$$

V_{mix} is the volume of surface water mixed with bottom water, V_{bot} is the volume of water in the bottom layer, $\Delta S°/_{oo}$ is the change in salinity in the bottom water, $\overline{S}°/_{oo}{}_{surf}$ is the average salinity of the surface water, and $S°/_{oo}{}_{init\ bot}$ is the initial salinity of the bottom water. Knowing the volume of surface water mixed daily into the bottom water, the loss of iron due to mixing across the thermocline can be calculated. There were deviations from linearity observed in the plot of salinity vs time. These deviations appeared to correlate with the times when large volumes of water were transferred from the tank for zooplankton sampling (~ 200 liters/ sampling period). Assuming a linear variation of salinity change with time gives the upper limit for the flux of iron across the thermocline due to mixing. During the course of this experiment a total of 0.109 moles of iron were added to the surface layer of the experimental tank (0.057 moles in the first experiment and 0.052 moles in the second experiment). The total iron loss from the surface layer due to mixing across the pycnocline was 1.64×10^{-3} moles; 0.86×10^{-3} moles of iron were lost in the first experiment and 0.78×10^{-3} moles in the second experiment. This constitutes < 1.5% loss of iron from the surface layer due to mixing.

4. DISCUSSION

The sequence of vertical profiles in the experimental tank can be used to construct a budget for the decay of the acid-iron waste in a stratified system. The waste addition to the experimental tank in the second experimental tank in the second experiment contained 0.052

moles Fe/kg. The total iron content of the water column at various times intervals during the second experiment was determined from a graphical integration of the time sequence of vertical profiles (Fig. 3). A mass balance of the total iron content of the water column 6 hr after the waste addition accounted fr 0.049 mole Fe/kg or 94% of the waste added. Within the next 20 hr there was a loss of ~ 50% of the waste from the water column (Fig. 6). The iron value observed 163 hr after the waste addition was anomalously high; this deviation is probably due to an inaccurate estimate of the background level of iron in the bottom layer of the tank at this time. An elevated iron level in the bottom layer suggested an input of iron from the sediments during this time period (Fig. 5).

The decay of iron from the water column was similar to the removal of iron from the surface layer (Fig. 6). For this comparison the iron concentration in the surface layer was normalized to the concentration observed 1 hr after the waste addition. These data suggest a first order kinetic removal process for both the surface layer and the entire water column. The rate constant (k_1 = 0.0196) and the half life (τ = 35.5 hr) calculated from these two data sets were identical. The largest deviation appears between 10 and 50 hr when there was an accumulation of the waste in the thermocline. The similarity of these two analyses suggests that the same process is removing the acid-iron waste from the bottom layer as from the surface layer. Visual observation of the particulate matter that accumulated in sediment traps suspended in the tanks below the thermocline showed that unperturbed particulate iron floc penetrated the thermocline.

There was no apparent accumulation of iron in the phytoplankton and zooplankton species exposed to the acid-iron waste during the time frame of the experiment (P. Donaghay, personal communication). From these observations we conclude that the removal of the iron from the water column is due to gravitational settling of the particulate iron floc and not due to the assimilation by organisms.

The results of the MERL study may be compared with those obtained from a field study of an acid-iron waste dump at DWD-106. The field data were obtained on a cruise in August, 1979 on the G. B. Kelez. The same acid-iron waste was used in both studies so that variation in the composition of the waste need not be considered. The acid-iron waste plume was tracked in the field for 15 hr; thus the time frame for comparison of the field study and observations in the MERL tank were limited. The iron concentration from the field study and the two MERL experiments were normalized to the concentration observed 1 hr after the waste addition to allow a direct comparison of the data. The rate of removal from the surface water in the field study at a depth of 3 m is comparable with the observations in the MERL tank. The removal of iron in the open ocean is faster than that observed in the tank study. These data are reasonable considering that there is both horizontal and vertical dispersion of the waste plume in the open ocean, whereas in the MERL tank there is only the vertical flux of waste in the water column. These data clearly indicate that the MERL system can approximate the vertical removal processes that occur in the ocean for this waste.

5. CONCLUSION

The MERL study allows us to better understand the behavior of the acid-iron waste in a pycnocline. In the course of the experiment we observe a depletion of iron in the surface layer with an accumulation at the thermocline during the first 50 hr after the waste addition. The half life of the acid-iron waste in the upper layer of the tank was 35 hr. The fate of the acid-iron waste after penetration through the thermocline is complicated by the role of sediment resuspension. However, the high concentration of chromium in the waste can be used to differentiate iron values associated with the acid-iron waste and those associated with benthic regeneration. A mass balance of the total iron content in the tank at several time intervals after the waste addition showed that the rate of iron removal from the entire water column was similar to that observed in the surface layer. Thus, the same mechanism, gravitational settling of the iron floc, is responsible for the decay of iron from the surface and bottom layers. The results of the MERL tank experiment were consistent with field studies of the actual acid-iron waste dump at DWD-106. This study demonstrates the applicability of a MERL tank experiment to simulate processes that occur in the open ocean.

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REFERENCES

Brewer, P. G. 1975. Minor elements in sea water. In: Chemical Oceanography, Vol. 1, 2nd ed., J. P. Riley and G. Skirrow, Eds. Academic Press, London, pp. 415-496.

Brown, M. F., D. R. Kester, and J. M. Dowd. 1982. Automated iron measurements after acid-iron waste disposal. In: Waste in the Ocean, Vol. 1: Chemical and Sewage Wastes, I. W. Duedall, D. R. Kester, B. H. Ketchum, and P. K. Park, Eds. Wiley-Interscience, New York, in press.

Csanady, G. T. 1981. An analysis of dumpsite diffusion experiments. In: Ocean Dumping of Industrial Wastes, B. H. Ketchum, D. R. Kester, and P. K. Park, Eds. Plenum Press, New York, pp. 109-129.

Klos, E. G. and P. Donaghay. 1982. Description and behavior of a MERL stratified microcosm. In preparation

Kester, D. R., R. C. Hittinger, and P. Mukherji. 1981. Transition and heavy metals associated with acid-iron waste disposal at Deep Water Dumpsite 106. In: Ocean Dumping of Industrial Wastes, B. H. Ketchum, D. R. Kester, and P. K. Park, Eds. Plenum Press, New York, pp. 215-232.

Mukherji, P. and D. R. Kester. 1982. Comparison of summer and winter acid-iron dump experiments at Deep Water Dumpsite 106. In: Wastes in the Ocean, Vol. 1: Chemical and Sewage Wastes, I. W. Duedall, D. R. Kester, B. H. Ketchum, and P. K. Park, Eds. Wiley-Interscience, New York, in press.

Stookey, L. L. 1970. Ferrozine - a new spectrophotometric reagent for iron. Analytical Chemistry, 42, 779-781.

Wilson, T. R. S. 1975. Salinity and the major elements of sea water. In: Chemical Oceanography, Vol. 1, 2nd ed., J. P. Riley and G. Skirrow, Eds. Academic Press, London, pp. 365-413.

Legend of Figures

Fig. 1. Physical configuration of MERL stratified microcosm

Fig. 2. Vertical temperature and salinity profile of the experimental tank; a) temperature profile, b) salinity profile.

Fig. 3. Vertical profile of the iron concentration in the experimental tank at several time intervals in the second experiment: a) background; b) 6 hr after waste addition; c) 20 hr after waste addition; d) 44 hr after waste addition; e) 92 hr after waste addition; f) 164 hr after waste addition.

Fig. 4. Decay of acid-iron waste from the surface layer of the experimental tank. a) Depletion of total iron in the surface layer of the experimental tank as a function of time after the waste addition in the first and second experiment. b) First order kinetic removal of iron from the suface layer of the experimental tank in the second experiment. Fe(I) = initial iron concentration; Fe(T) = iron concentration after time, T.

Fig. 5. Comparison of the accumulation of Fe and Cr in the bottom layer of the experimental tank during the first and second experiments. a) Variation in T(Fe) as a function of time after the addition of the acid-iron waste . b) Variation in T(Cr) as a function of time after the addition of the acid-iron waste.

Fig. 6. Comparison of the removal of iron from the experimental tank during the second experiment: ▭ = removal from the suface layer normalized to the iron concentration observed 1 hr after waste addition; ◇ = iron removal calculated from a mass balance of the entire tank. (Iron values expressed as % of iron accounted for in mass balance.)

Fig. 7. Comparison of the rate of removal of iron in the MERL tank experiment and from field studies in September, 1979 on the G. B. Kelez.

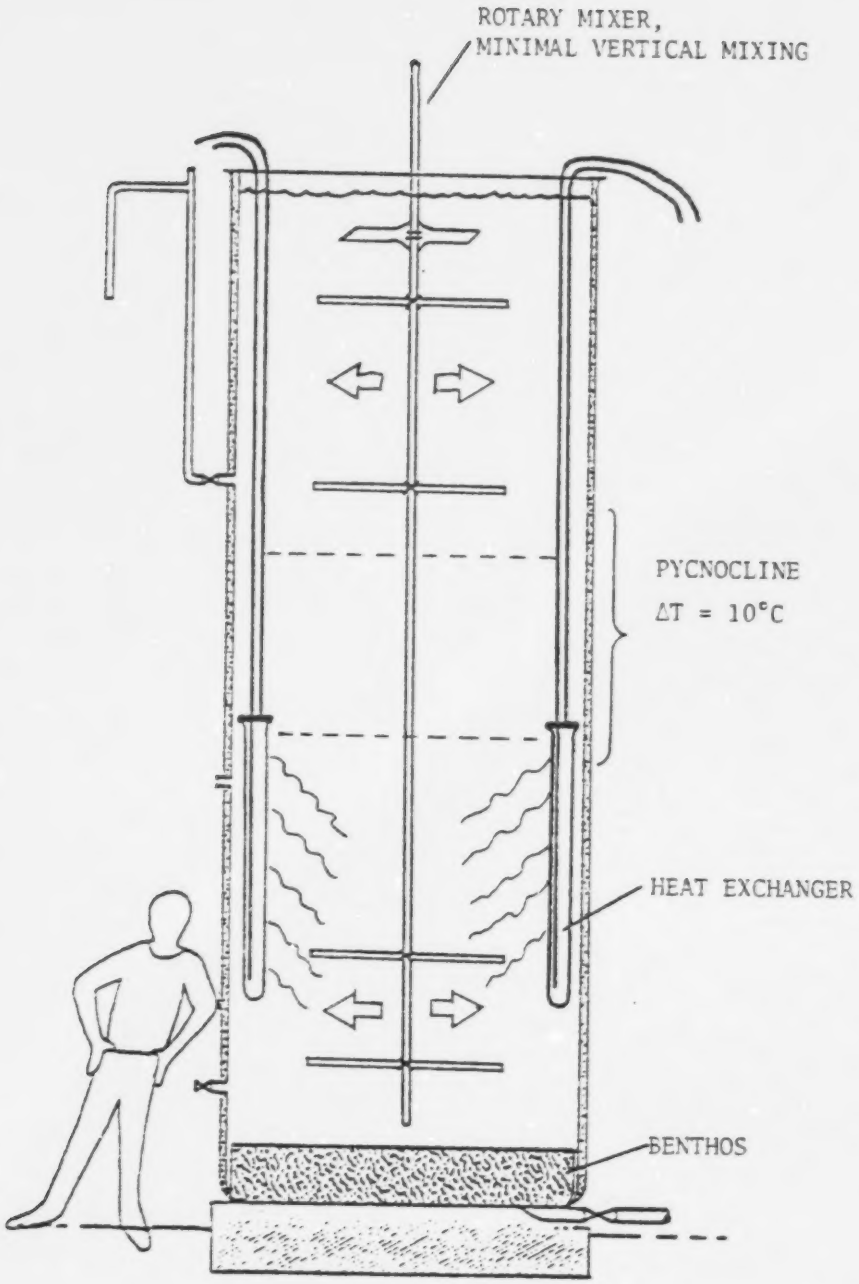
ROTARY MIXER,
MINIMAL VERTICAL MIXING
PYCNOCLINE
ΔT = 10°C
HEAT EXCHANGER
BENTHOS

Fig. 1.

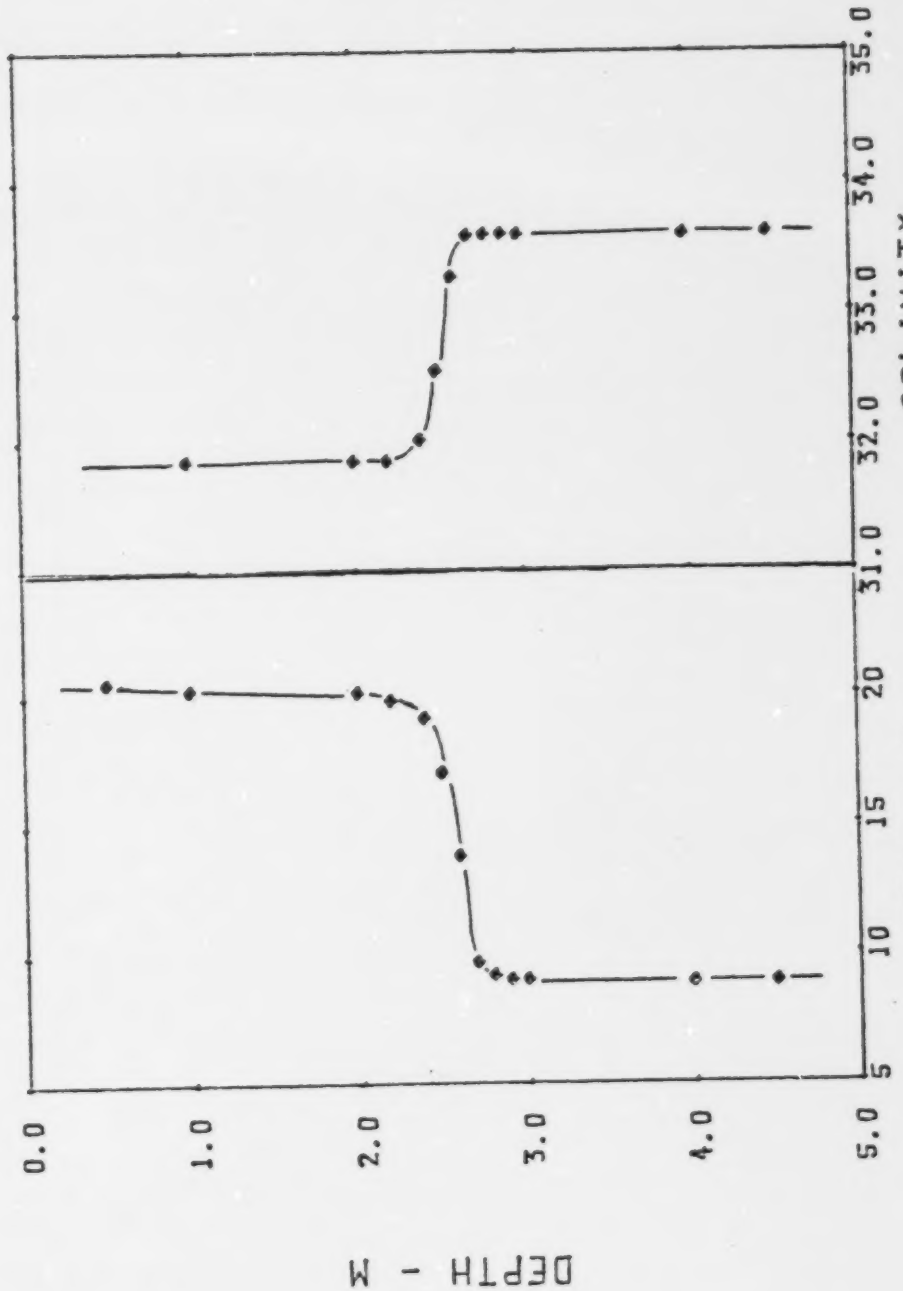
DEPTH - M
0.0
1.0
2.0
3.0
4.0
5.0
5
10
15
20
TEMP - C
31.0
32.0
33.0
34.0
35.0
SALINITY

Fig 2a

Fig 2b

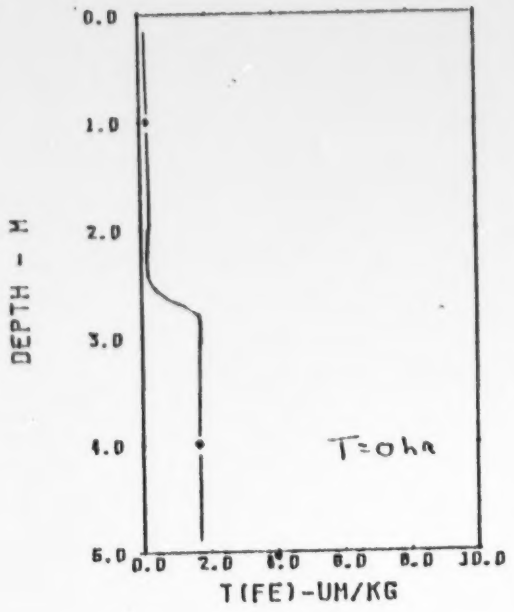

Fig 3a

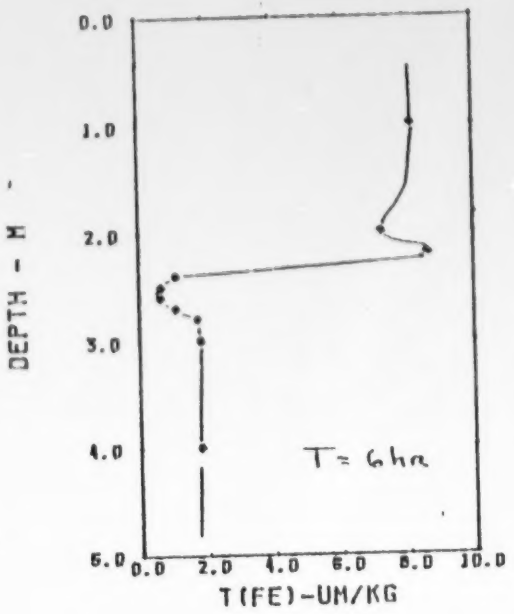

Fig 3b

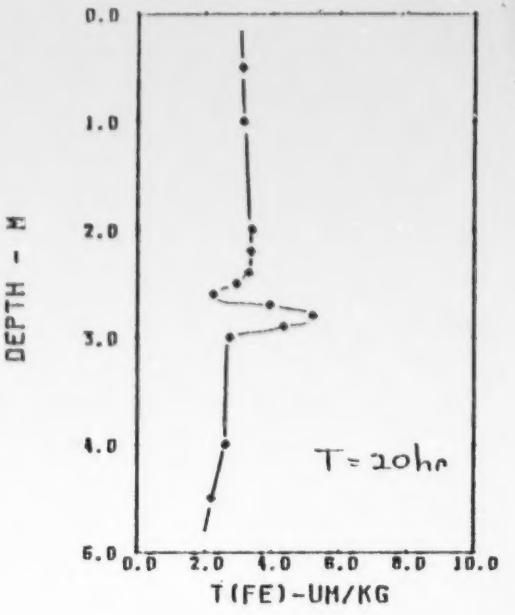

Fig 3c

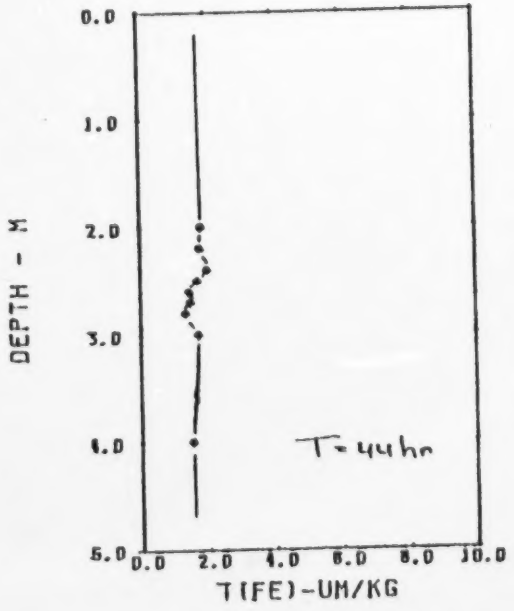

Fig 3d

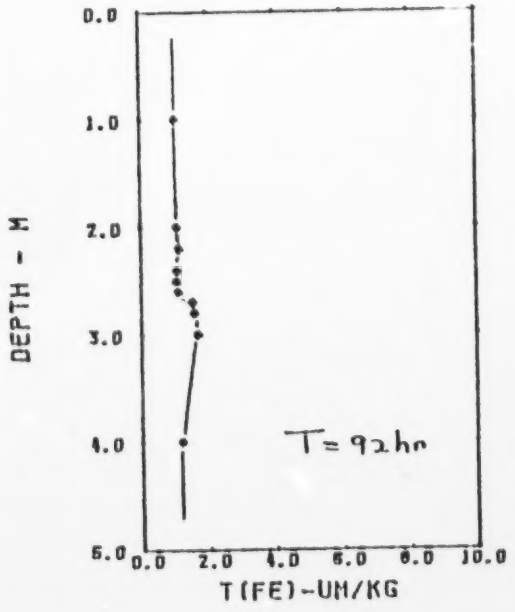

Fig 3e

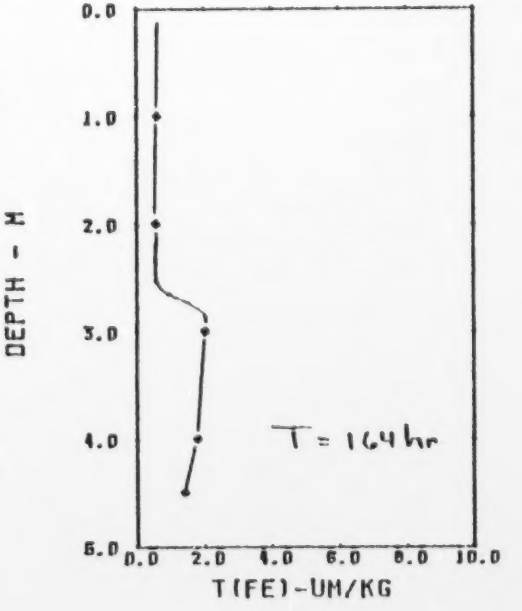

Fig 3f

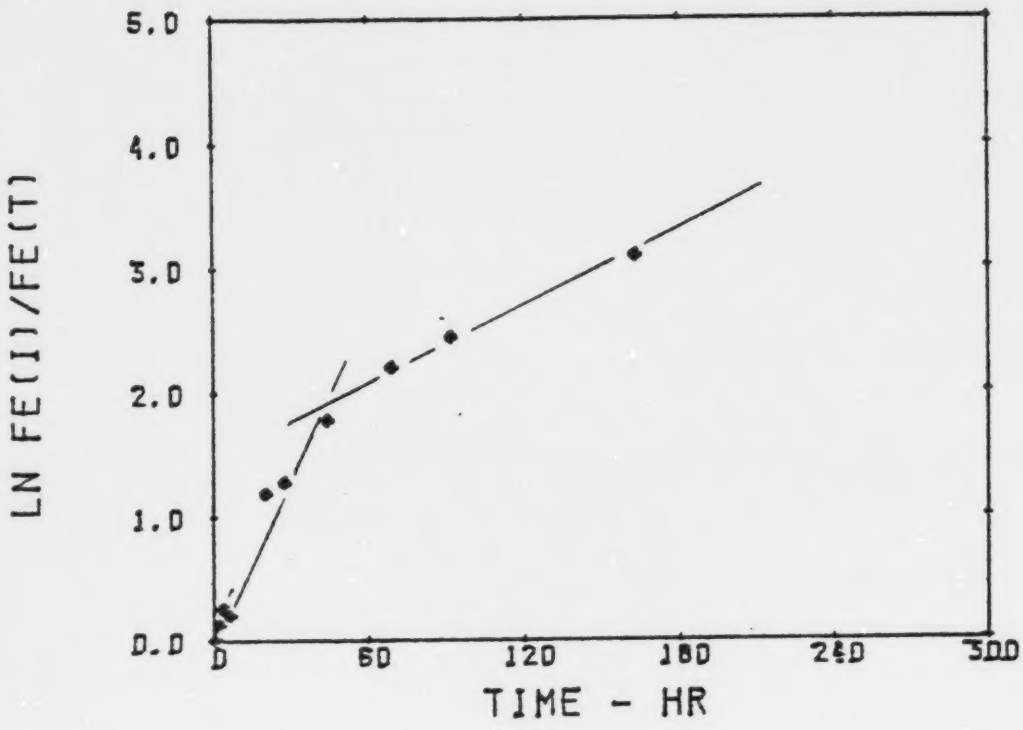
LN FE(I)/FE(T)
5.0
4.0
3.0
2.0
1.0
0.0
0
60
120
180
240
300
TIME - HR

Fig 4b

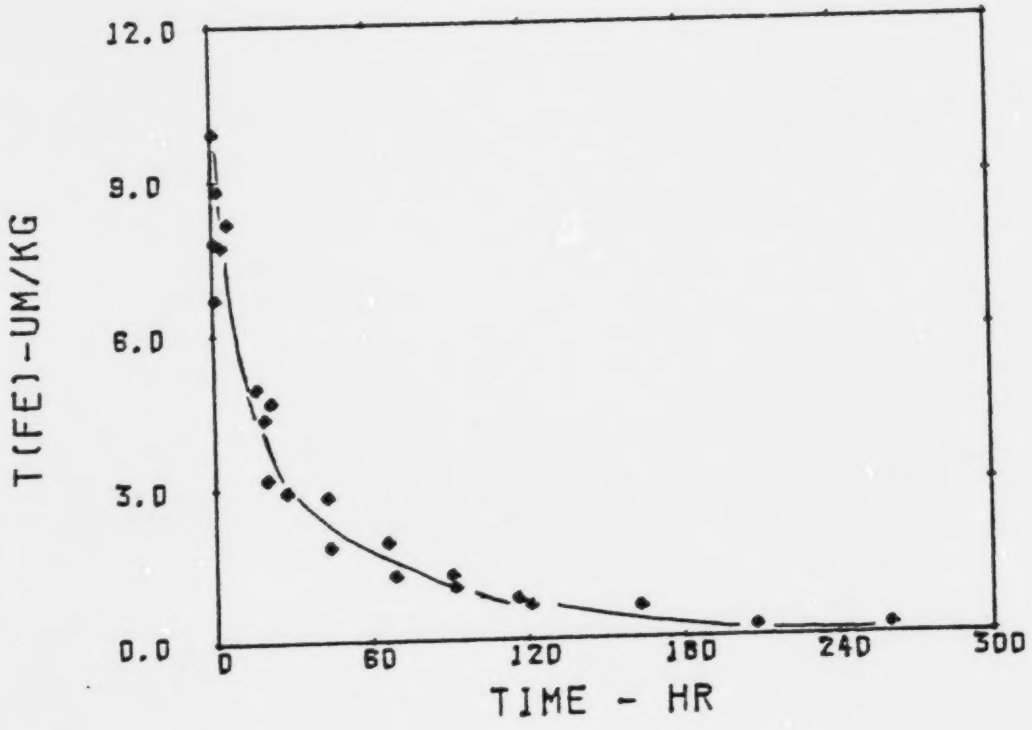
T(FE)-UM/KG
12.0
9.0
6.0
3.0
0.0
0
60
120
180
240
300
TIME - HR

Fig 4a

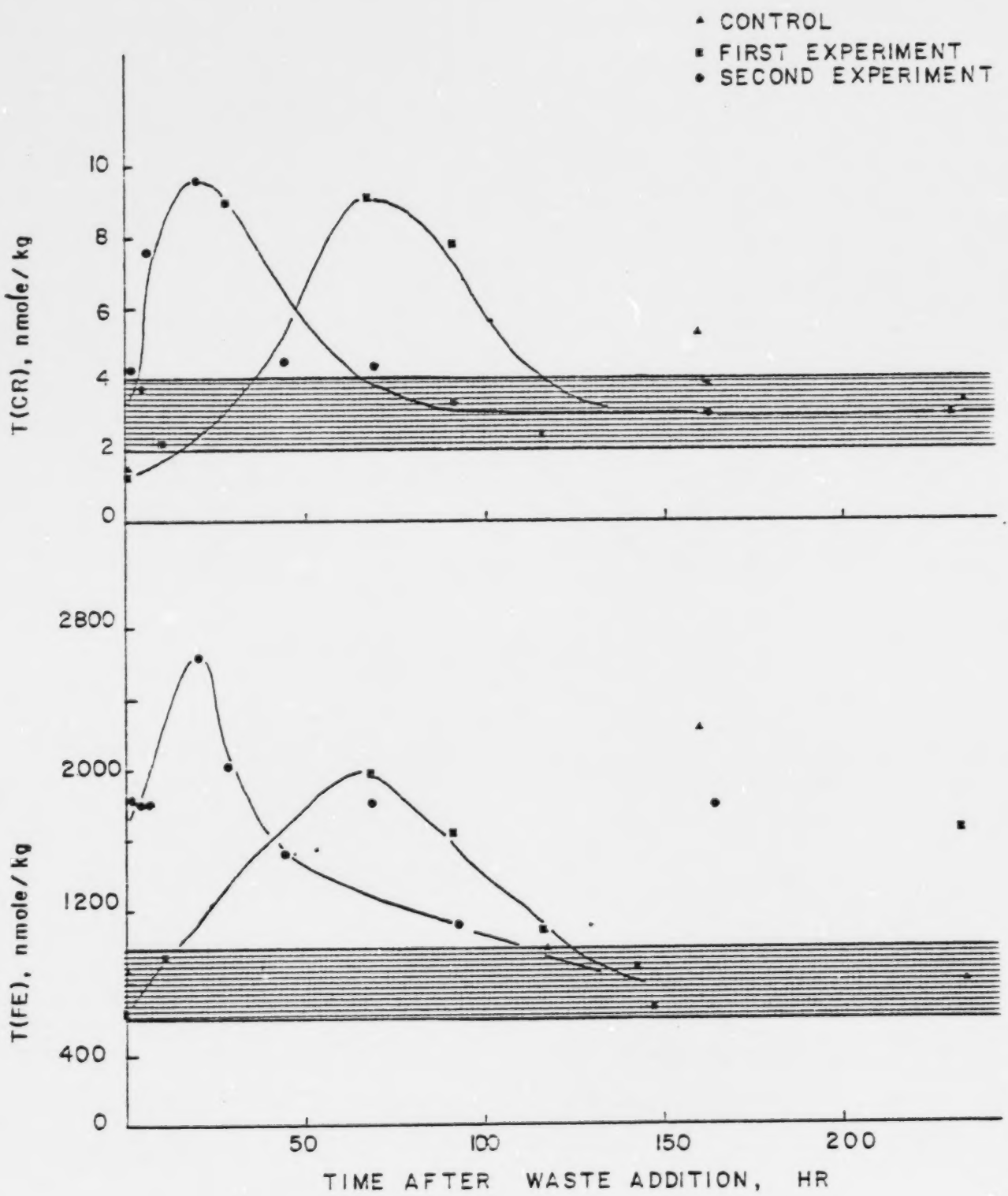
▲ CONTROL
▪ FIRST EXPERIMENT
• SECOND EXPERIMENT
T(CR), nmole/kg
10
8
6
4
2
0
T(FE), nmole/kg
2800
2000
1200
400
0
50
100
150
200
TIME AFTER WASTE ADDITION, HR

Fig 5

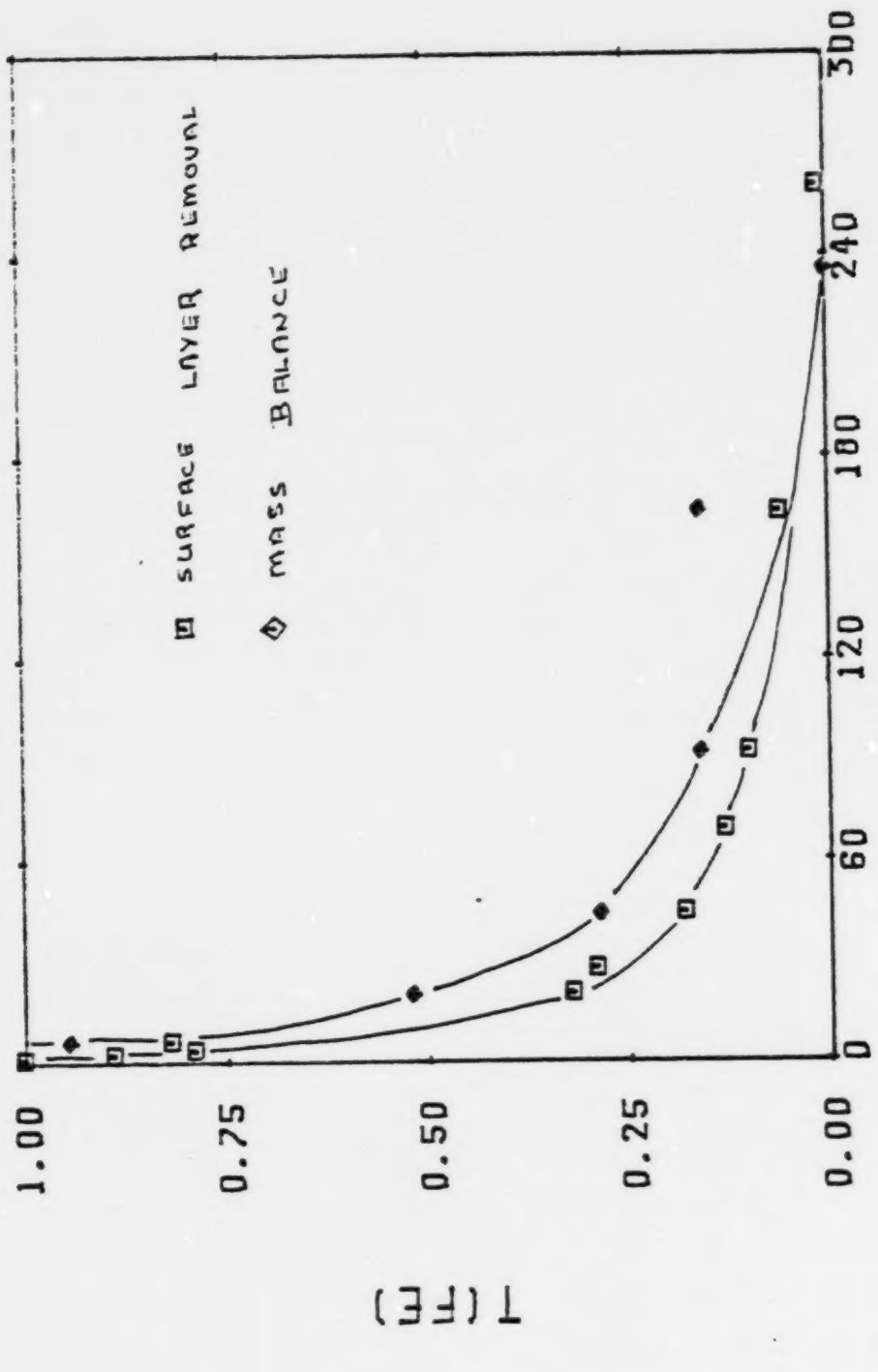
SURFACE LAYER REMOVAL
MASS BALANCE
1.00
0.75
0.50
0.25
0.00
0
60
120
180
240
300
TIME - HR
T (FT)

Fig 6

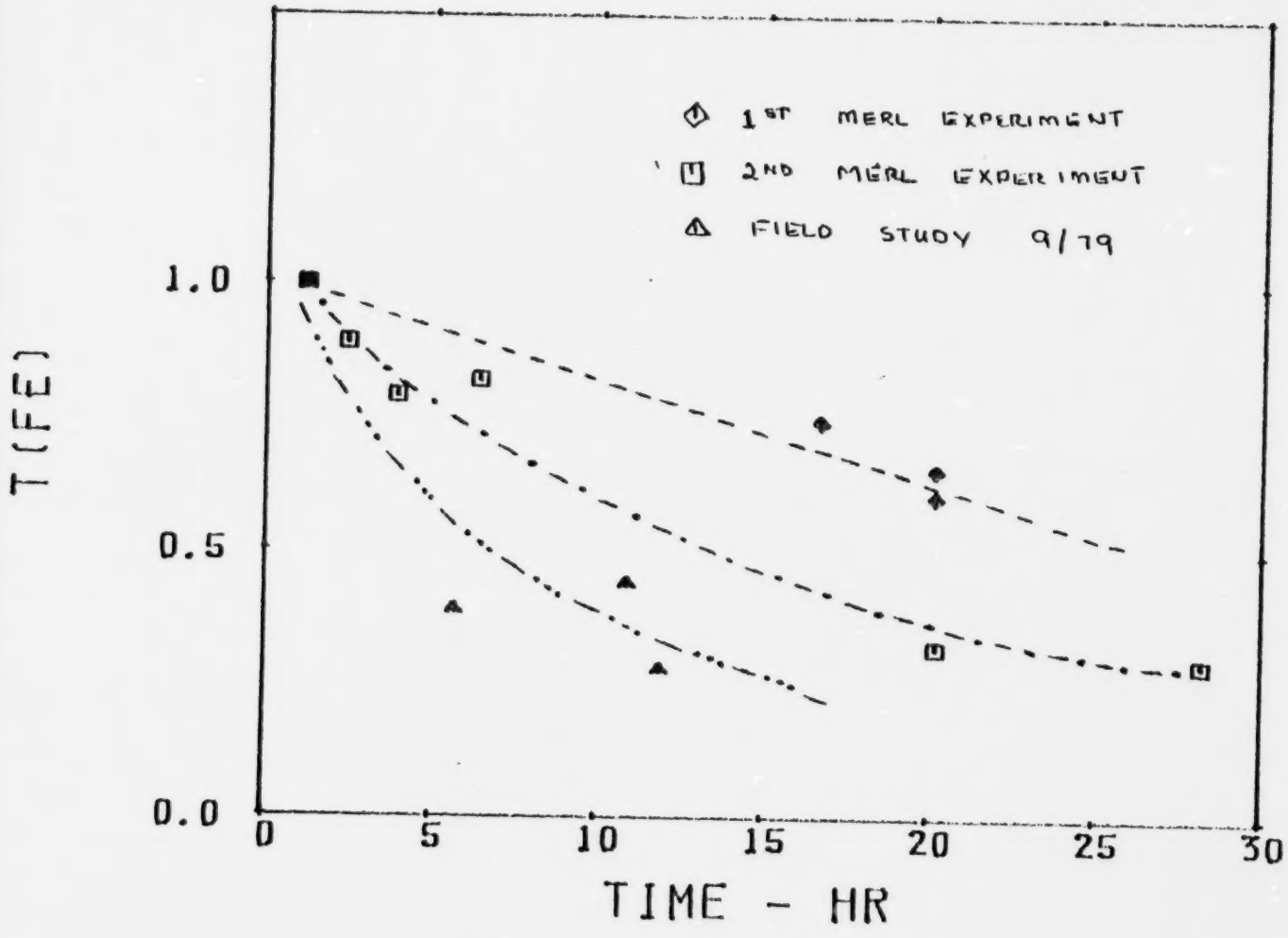
1ST MERL EXPERIMENT
2ND MERL EXPERIMENT
FIELD STUDY 9/79
T (FE)
1.0
0.5
0.0
0
5
10
15
20
25
30
TIME - HR

Fig 7